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TiO_2/Fe_2O_3 CORE SHELL THIN FILM FOR PHOTOVOLTAIC APPLICATION

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Nanocrystalline core – oxide shell thin film of TiO_2/Fe_2O_3 was deposited using the simple and inexpensive chemical bath deposition technique within the pores of polyvinyl alcohol. The film was studied for possible application in photovoltaic architecture, by characterizing the films using X-ray diffractometer, Scanning electron microscope, and UV– ViS spectrophotometer and four point probe. The effect of post annealing on some properties of the thin film was also investigated. The optical band gap energy, calculated from the absorption spectra, was found to be in the desired interval to be applied as solar absorber material for photovoltaic architecture.

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1. Introduction

Solar energy is one of the most available, non - conventional energy resources with promising features to be considered for power requirements of the 21st century especially in the tropics. The studies of semiconductor nano particles have shown that they poses many new areas of applications, such as in solar cells, photo detectors, LEDS and switches [1,2]. Energy conversion in solar cell consists of generation of electron – hole pairs in semiconductors by the absorption of light and separation of electrons and holes by an internal electric field. Charge carriers collected by two electrodes give rise to a photocurrent when the two terminals are connected externally [3]. The spectrum of solar energy spans from the UV (300nm) to the infrared region (3000nm). When a semiconductor material absorbs this photon energy, the electron at the valence band are excited to the conduction band provided the photon energy is greater or equal to the energy band gap. This process results in the creation of electron – hole pair [4].

A hetero-junction is normally formed by joining two layers of semiconductor material with differing band – gap energies. If the layer so formed has the same conductivity, an isotype hetero-junction is formed. However if the reverse is the case, an anisotype heterojunction is formed. The requirement to get appropriate band – gap energies for device application has led to the development of binary, ternary and quaternary thin films [5, 6].

In recent years, the development of core/shell structured materials on a nanometer scale has been receiving extensive attention [7, 8]. The shell can alter the charge, functionality and reactivity of the surface, or improve the stability and dispersive ability of the core material [9].It is also believed that optical, catalytic or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell structured thin films has the advantage of obtaining a new composite material having synergetic or complementary characteristics of the composites. Many studies on the synthesis of composites, i.e. TiO_2, [10], $CaCO_3$ [11], γ-Fe_2O_3 [12] and Ag coated with SiO_2 have been reported.

In this paper, we report the chemical bath deposition of TiO_2/Fe_2O_3 core- shell thin films and the analysis of the band gap and optical transmission for possible application in solar cell architecture.

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2. Experimental details

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following order. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA and stirred at 363K for 60mins. The solution was aged until the temperature dropped to room temperature. To obtain the deposition of TiO_2, the chemical bath was composed of 12mls of 1M $TiCl_2$, 12mls of 1M $NH4Cl_4$, 12mls of 10M NH_3 and 13mls of PVA solution put in that order in 100ml cleaned and dried beaker. Four (4) clean glass slides were then inserted vertically into the solution. The deposition was allowed to proceed at a temperature of 338K for 3hrs in an oven after which the coated substrate were removed, washed with distilled water and allowed to dry. To obtain the TiO_2/ Fe_2O_3 core-shell, the TiO_2 film already formed (core) was inserted in a mixture containing 13 ml of 1M KCL, 2 drops of 1M NaOH and 50mls of water in 100ml beaker. Deposition was allowed to proceed at same temperature and duration. The deposited films were annealed in an oven between 373K and 673K respectively for 1hr. One of the samples was left unannaeled to serve as the control. The surface morphology of the films was observed by scanning electron microscopy (SEM) with JEOL 35C instrument, the energy used was 10 kV. The X-ray diffraction (XRD) studies were carried out in a Rigaku D/max-2100 diffractometer ($CuK\alpha_1$ radiation, 1.5408Å) in the 2θ range of 20^0 - 75^0 with a thin film attachment. The chemical composition of the thin film was determined using Energy dispersive X-ray Fluorescence. The ultraviolet-visible (UV-Vis) spectra of the films were measured on Perkin-Elmer Lambda-2 spectrometer, in 200-1200 nm wavelength range. The transmission was measured using glass as a reference sample. Four point probes were employed to measure the resistivity of the sample.

3. Results and discussion

Fig.1 shows the XRD pattern of the $Ti0_2/Fe_20_3$ film deposited in this work. The samples were annealed from 373K to 673K for 1 hour. This was done to improve upon the intensities of the peaks crystallinity of the films and to investigate the effect of post annealing on the deposited films.

The peak at 2θ value of 19.78 and are attributed to orthorhombic TiO_2 (JCPD card No.35-0088) having lattice parameters a = 9.7965 Å, b= 9.980 Å and c=3.7301 Å these were assigned to the diffraction lines produced (200) and (111) planes. However the additional peaks at an angle of 19.36 and 22.15 are identified to be Fe_20_3 (JC PD Card No.41-1432) and assigned to the diffraction line produced by (200) and (111) planes of the Fe_2O_3 – plane. These results suggest that the thin film deposited in this work is a mixture of the two oxides. The XRD pattern also revealed that the annealed film has better crystallinity as is evident in Fig. 2. The average crystallite size of the film was calculated from the recorded XRD patterns using the Scherer formula: $D = 0.89\ \lambda/\beta\ Cos\theta$ [8], where D is the average crystallite size, λ is the wavelength of the incident x – ray, β is the full width at half maximum of X – ray diffraction and θ is the Bragg's angle.

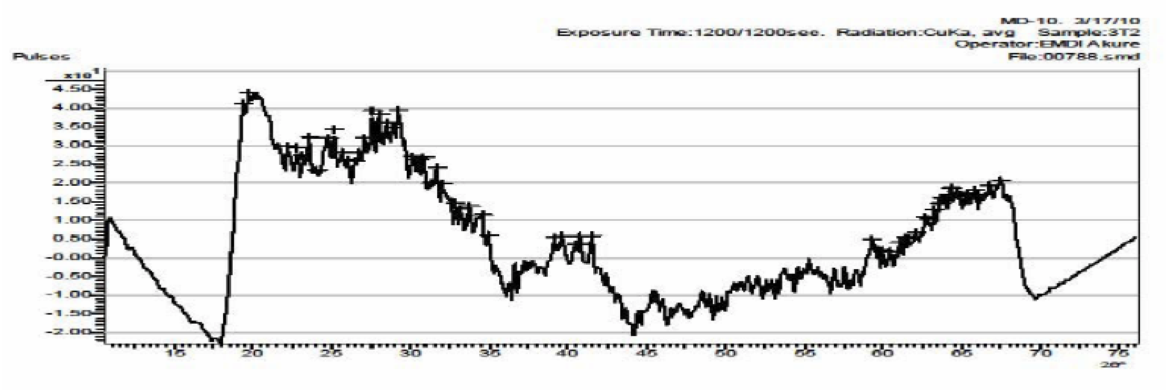


Fig. 1. X ray diffraction of TiO_2/Fe_2O_3 thin film as deposited

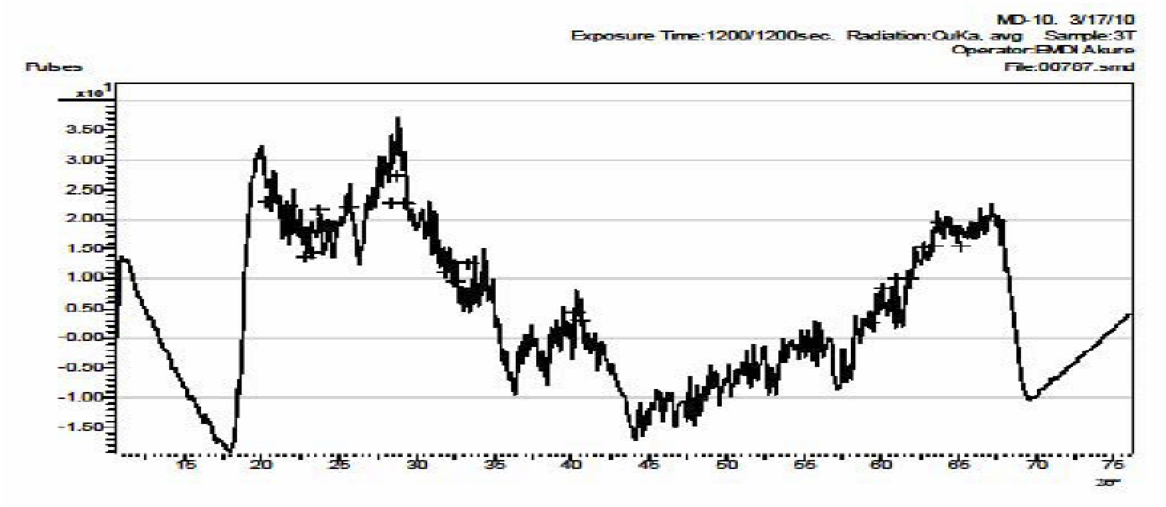
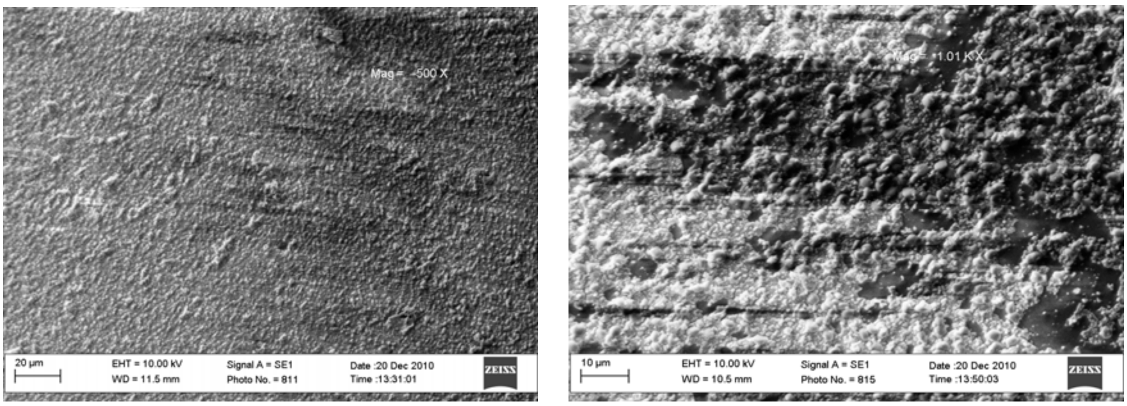


Fig. 2. X-ray diffractogram of TiO_2/Fe_2O_3 at 673K.



(a) (b)

Fig. 3. SEM of TiO2/Fe2O3 as-deposited (b) annealed at 673K

The average crystallite size of the deposited film was found to be 2.65Å. Fig.3 shows the SEM of TiO_2/Fe_2O_3 thin film. Uniform distribution of the grain is observable with gradual fading in colour from gray to yellowish brown. The SEM show a decrease in grain size at higher annealing temperature due to effects of evaporation of absorbed water and reorganization of the grain. The optical absorption spectra of the film were studied in the range of wavelength 200nm – 1200 nm. The variation of absorbance (A) and percentage transmittance (%T) with wavelength for all the samples of the film under study are show in fig.4 and 5 respectively. Thin film of TiO_2/Fe_2O_3 show better absorbance in the visible region and a lower absorption in the IR of the solar spectrum with a peak absorbance of 1.5. The absorbance decreases exponentially with wavelength for the entire sample annealed at different temperature. A sharp decrease in absorbance was noticed for the entire sample at a wavelength of 800 nm.

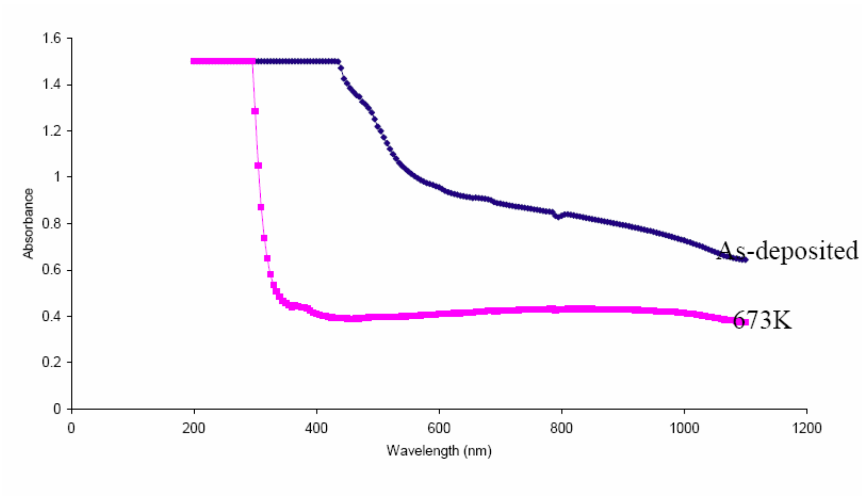


Fig. 4. Absorbance vs. wavelength for TiO_2/Fe_2O_3 *for as-deposited and annealed at 673K*

Fig.5 shows the transmittance plot for the deposited thin film. The plot shows that the films transmit well in the wavelength range opposite to that of the absorbance. With the decreasing wavelength of radiation, the transmittances of all the thin films tended to be lowered. This was consistent with the report that absorption coefficient of some thin film increased with increasing photon energy. This implies that films that absorb well in the IR region transmit poorly in the same region. The spectral distribution of figures 4 and 5 show that the films deposited in this work could be used as spectrally selective window coatings in cold climate to facilitate transmission of ViS and NIR while suppressing the UV portion of solar radiation. The films can be used for making sun glasses for protection from sun burn caused by UV radiations.

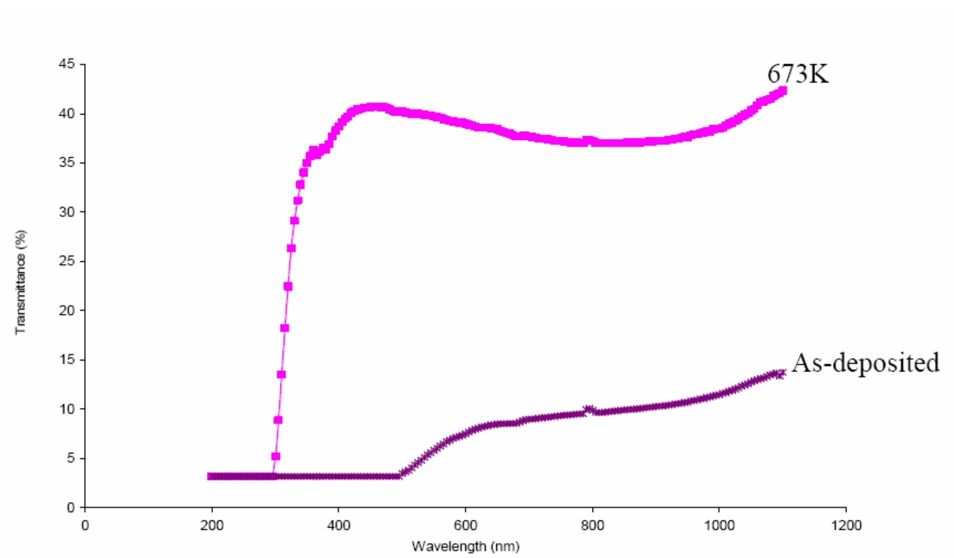


Fig. 5.Transmittance vs. photon energy for as-deposited and annealed at 673K.

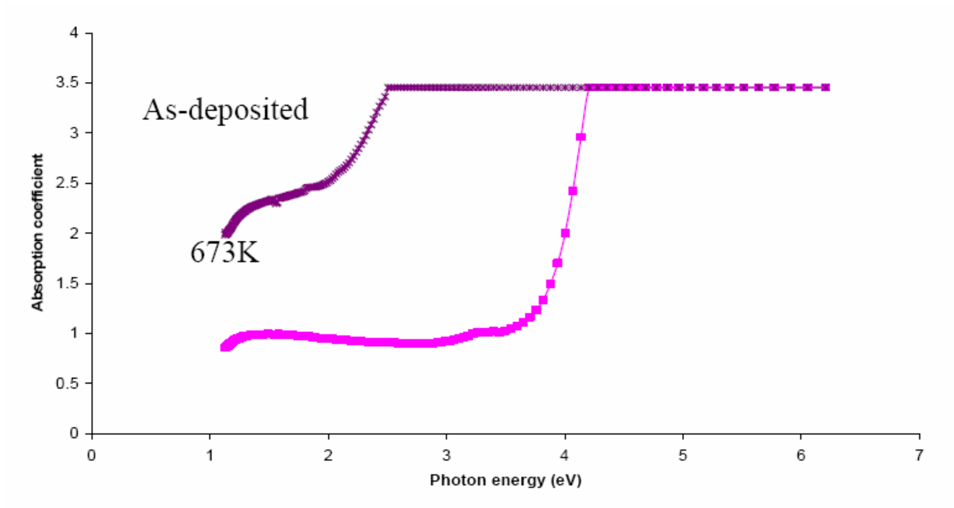


Fig. 6. Absorption coefficient vs. photon energy for as-deposited and annealed at 673K

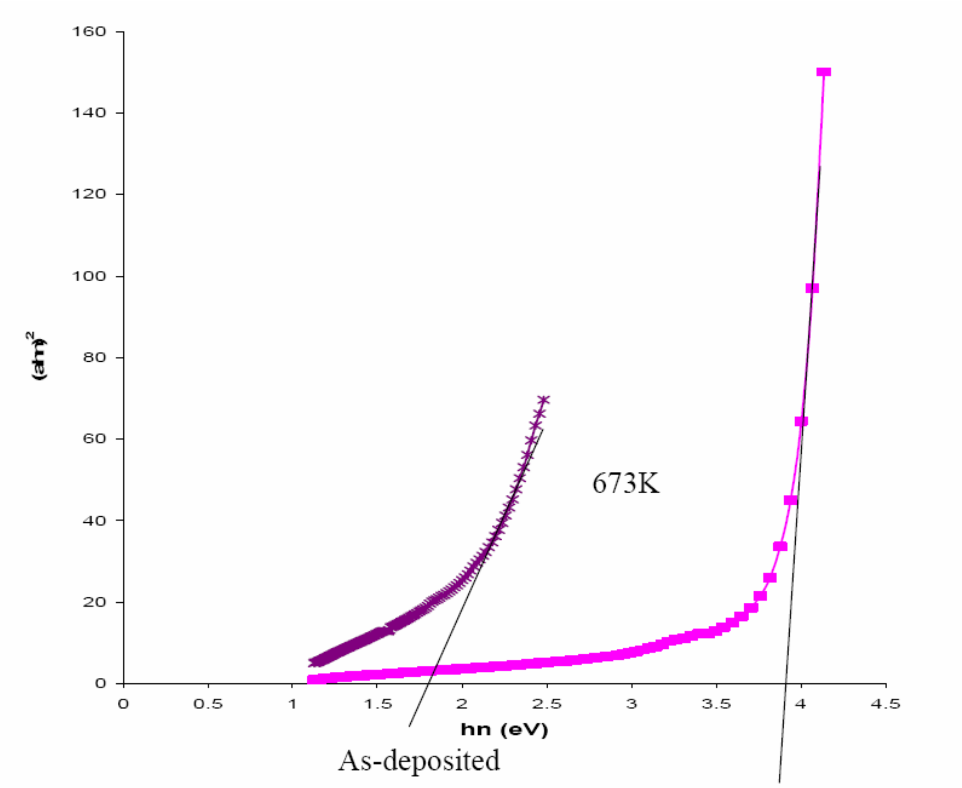


Fig.7. $(\alpha h\upsilon)^2$ *vs.* $h\upsilon$ *for* TiO_2/Fe_2O_3 *for as-deposited and annealed at 673K*

The details of the mathematical determination of the absorption coefficient (□) can be found in literature [13] while the plot of absorption coefficient against photon energy is displayed in fig.6. The plot of ($\alpha h\nu$) versus *hv* shown in Fig.7 is linear and indicates the presence of direct transition. The straight portion is extrapolated to energy axis at $\alpha = 0$ which gives the band gap energy *E*g of the thin film to be 1.80 eV and 3.9 eV respectively at temperatures of 273 K and 673 K. The energy gap E_g was calculated using the relation $(ah\upsilon)^2=A(h\upsilon - E_g)^n$

Where A is a constant, hv is the photon energy of the incident light, n is an integer which depends on the nature of transition. For direct transitions n = ½ or 2/3 while for indirect n = 2 or 3 depending on whether they are allowed or forbidden respectively. The estimated values of the direct energy bad gap from fig. 7 for the deposited film lies in the range of 2.0 - 3.9ev. As well, the as-deposited film presents lower E_g values than the annealed one. This can be attributed to an increase in the carrier concentration due to the presence of Fe and its electrical activation probably improved by the annealing process, which decreases the potential barrier between grains. The annealing process has been noted to be helpful in improving the electro-optical properties of thin films [8]. This is attributed to better crystalline quality and oxygen deficiency after annealing, however, the effect of these processes is still not well known

A material with a high bad gap of 3.9 eV and high absorption coefficient of more than 10^{-4}cm^{-1} has been regarded as a promising absorber for thin film photovoltaic applications [1]. The high energy gap implies that the thin film can be used for wide variety of applications in solar architecture.

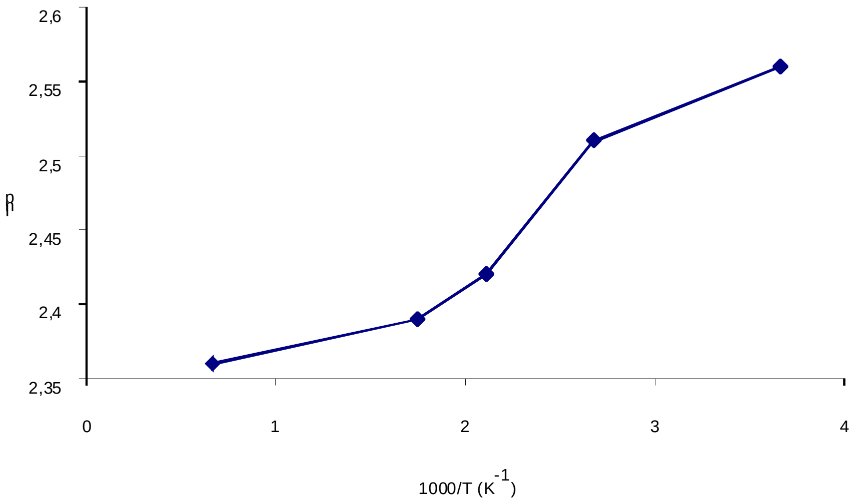


Fig.8. Variation of electrical resistivity with temperature.

3.1 Electrical property

The electrical resistivity of T_iO_2/F_eO_3 film (thickness: 840 nm) on glass substrate was measured by conventional d. c. two-probe method in the range of 273–673K of temperature. The as-deposited film has electrical resistivity of the order $2.56\text{x}10^{-8}$ Ωm while the film annealed at 673K has a resistivity of the order of 2.36×10^{-8} Ωm. Variation of electrical resistivity (logρ) with reciprocal of temperature (1000/*T*) for annealed thin film decreased with temperature indicating the normal semiconductor behaviour. The decrease in resistivity can be attributed to the substitution of Ti^+ ions at Fe^{3+} sites leaving free ions. It is also known that the main factor affecting the resistivity of thin films especially the oxides are interstitial oxygen vacancies. The activation energy was calculated using the relation $\rho = \rho_o \exp\frac{E_a}{KT}$. For thin film annealed at 673K the activation energy is 0.35 eV.

4. Conclusions

TiO_2/Fe_2O_3 thin films have been successfully deposited on a glass substrate at a temperature of As revealed by XRD measurement, TiO_2/Fe_2O_3 films are found to have simple with a preferred orientations of (200) and (100). Optical absorption measurements indicate the as deposited film has a direct band gap of 1.8 eV, while the film annealed at 673 K has a direct band gap of 3.9 eV suggesting that the band gap increases with increase in temperature. Annealing at higher temperatures decreases the resistivity of TiO_2/Fe_2O_3.

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